

CHAPTER III

THEORY

Catalytic oxidation can be categorized as complete oxidation and selective oxidation. Complete oxidation is the combustion of organic compound to the combustion products; CO_2 and H_2O [Thammanokul (1996)]. It is a practicable method for elimination of organic pollutants in gaseous streams. While selective oxidation is the reaction between hydrocarbon and oxygen to produce oxygenates (such as alcohols, aldehydes, carboxylic acids which are produced from partial oxidation processes) or unsaturated hydrocarbons (such as ethene and propene which can be produced from oxidative dehydrogenation process) [Thammanonkul (1996)].

Satterfield (1991) has summarized the behavior of the oxidation reaction as follow:

In the manufacture of organic chemicals, oxygen may be incorporated into the final product, as in the oxidation of propylene to acrolein; or the reaction may an oxidative dehydrogenation in which the oxygen does not appear in the desired product, as in the conversion of butene to butadiene. The desired reaction may or may not involve C-C bond scission. Closely relate reaction is ammoxidation reaction in which a mixture of air or ammonia is reacted catalytically with an organic compound to form a nitrile.

In studies on oxidative catalysis; commonly great attention is attached to the state of oxygen on the catalyst surface. A relatively inert oxygen molecule is activated by interacting with the surface of oxide catalyst. The main parameter determining oxygen reactivity on the catalyst is energy of oxygen binding with the catalyst as a thermochemical characteristic. Correlation between rates of catalytic oxidation and oxygen binding energy on oxide catalysts have been established. The weaker the oxygen binding with the catalyst surface, the more efficient is complete oxidation with this catalyst.

In partial oxidation reactions, it usually necessitate H atom(s) abstraction, and O atom(s) insertion from the surface into the hydrocarbon molecule and several electron transfer. In the well accepted Mars and van Krevelen mechanism, lattice oxygen anions are assumed to be inserted in the substrate molecule or to facilitate its dehydrogenation by forming H₂O while the metallic cations inserted the redox mechanism to occur by changing their oxidation state. This was postulated that the catalytic reaction comprises two steps.

It has been reported that maximum selectivity is associated with an optimum degree of oxygen mobility. For an optimum selectivity combination of activity and selectivity there should be matching between the difficulty of oxidizing the reactant and the ease of removal oxygen from the catalyst. Tightly bond oxygen should result in a low activity catalyst. High mobile oxygen should result in a high activity catalyst, but one that is nonselective.

There are several problems in pressing oxygen mobility very far as a useful concept. The approach is perhaps most useful in considering a very broad range of catalyst composition, but many other factors are involved. For high selectivity in a reaction of the type $A \rightarrow B \rightarrow C$ it is necessary that the rate of desorption of a desired intermediate B be high relative to the rate of further oxidation. This is related to the strength of adsorption of B, which is determined by other aspect of catalyst structure.

With oxide catalysts, chemisorbed surface oxygen as well as lattice oxygen may play a role. The oxidation of propylene to acrolein on a BiMo/SiO₂ catalyst in a pulsed reactor showed by isotopic oxygen studies that surface chemisorbed oxygen as well as lattice oxygen could contribute to the overall reaction. It seem plausible that in many other cases chemisorbed oxygen would lead to a different set of products than lattice oxygen and both mechanisms could be significant. On the basis of other studies advanced the hypothesis that surface-adsorbed oxygen may in general lead to products of complete oxidation and that lattice oxygen is needed for partially oxidized products, but more study is needed to test this proposal.

3.1 Redox mechanism

The behavior of most oxidation catalysts can be interpreted within the framework of a redox mechanism. This postulates that the catalytic reaction comprises two steps.

1). Reaction between catalyst in an oxidized form, Cat-O, and the hydrocarbon R, in which the oxide becomes reduced.



2). The reduced catalyst, Cat, becomes oxidized again by oxygen from the gas phase.



Under steady-state conditions the rate of the above two steps must be the same. This mechanism was first proposed by Mars and van Krevelen in 1954.

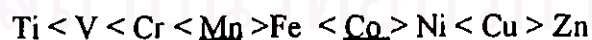
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3.2 Cobalt oxide catalyst

Cobalt oxide is an interesting material in the fields of heterogeneous catalysis. Among the transition metal oxides Co_3O_4 shows the highest catalytic activity for the combustion of organic compounds, CO, and ammonia. This is the reason why Co_3O_4 and Co-containing mixed oxides are normally included in the formations of catalysts for treatment of waste gases and are of interest in view of the development of methane catalytic combustion technology for energy supply. In addition, it is also active for hydrogenation and hydrodesulphurization reaction [Busca *et al.* (1990)].

Co_3O_4 is a black material having the structure of a normal spinel; it is thermodynamically stable up to 900°C with respect to the lower oxide CoO. This implies that Co_3O_4 is the oxide stable under the conditions of catalytic oxidation. Both Co_3O_4 and CoO are readily reduced to the metal in the hydrogen flow near 300°C . The surface of Co_3O_4 shows Co^{3+} ions in excess. This surface is very reactive, even with respect to a stable molecule such as ammonia and methanol, which are readily decomposed at room temperature [Busca *et al.* (1990)].

For the gas-phase oxidation of hydrogen, ammonia, methane, ethylene, propene, carbon monoxide, or toluene, the order of activity varied somewhat with the reactant, but the general pattern of activity found was [Satterfield (1991)].



In almost all cases the most active catalyst was cobalt oxide and manganese oxide; the least active were the oxides of titanium or zinc.

Co_3O_4 is very active in propane and propene catalytic combustion. FTIR studies suggest that adsorbed isopropoxide species and adsorbed acetone and acetates are intermediates in propane oxidation while adsorbed acrolein and acrylates are intermediates in propene oxidation. Co_3O_4 is also an active and selective catalyst for the oxydehydrogenation of propan-2-ol to acetone at low conversion, suggesting that

the same oxygen species involved in the total and partial oxidation of organic compounds. The catalyst behaved according to a Mars and Van Krevelen type mechanism. The activity of Co_3O_4 was attributed to nucleophilic oxygen species at the surface, associated with the presence of trivalent cobalt [Finocchio *et al.* (1997)]. Mechanism for propane and propene oxidation on Co_3O_4 was proposed in figure 3.1 and figure 3.2, respectively.

3.3 Effect of support on catalytic performance

Many researches found that the catalytic performance of catalyst depending on the type of support. Suitable support could improve catalytic activity of catalyst. For the oxidative dehydrogenation of propane, MgO was used as support for V_2O_5 catalyst which showed high catalytic performance in the oxidation of propane, giving ca. 20% conversion with about 60% selectivity to propene. It is suggested that the loading of V_2O_5 catalyst on metal oxide having solid-base properties or the formation of complex metal oxide between V_2O_5 and basic metal oxides, reduce the strong oxidation ability of V_2O_5 to attain higher selectivity to oxidative dehydrogenation [Chaar *et al.* (1988)]. The catalytic performance of molybdate catalyst was changed when MgO was loaded and it turned out that $\text{Mg}_{0.95}\text{MoO}_x$ catalysts having slight excess molybdenum showed the highest activity in the oxidative dehydrogenation of propane, which gave 61% selectivity to propene at 22% conversion of propane at 515°C . It was also revealed that the lattice oxide ions of the catalysts participated is an active oxygen in the oxidative dehydrogenation of propane [Yoon *et al.* (1995a)]. Metal molybdate catalysts were found to mostly promote the oxidative dehydrogenation of propane to propene. More than 80% selectivity to propene was attained on each catalyst but their catalytic activities differed greatly. Cobalt molybdate showed the highest catalytic performance for the oxidative dehydrogenation and the catalytic property strongly depended on the catalyst composition. $\text{Co}_{0.95}\text{MoO}_x$ catalyst gave 60% selectivity to propene at 20% conversion of propane at 450°C [Yoon *et al.* (1995b)].

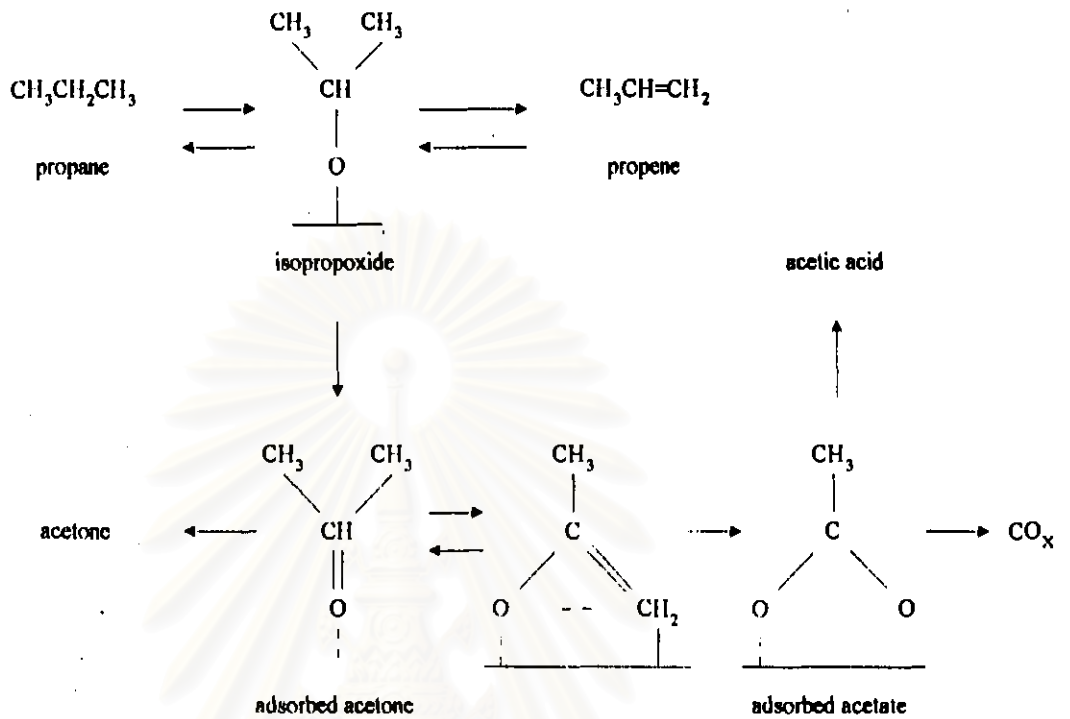


Figure 3.1 The oxidation path of propane over Co_3O_4 catalyst.

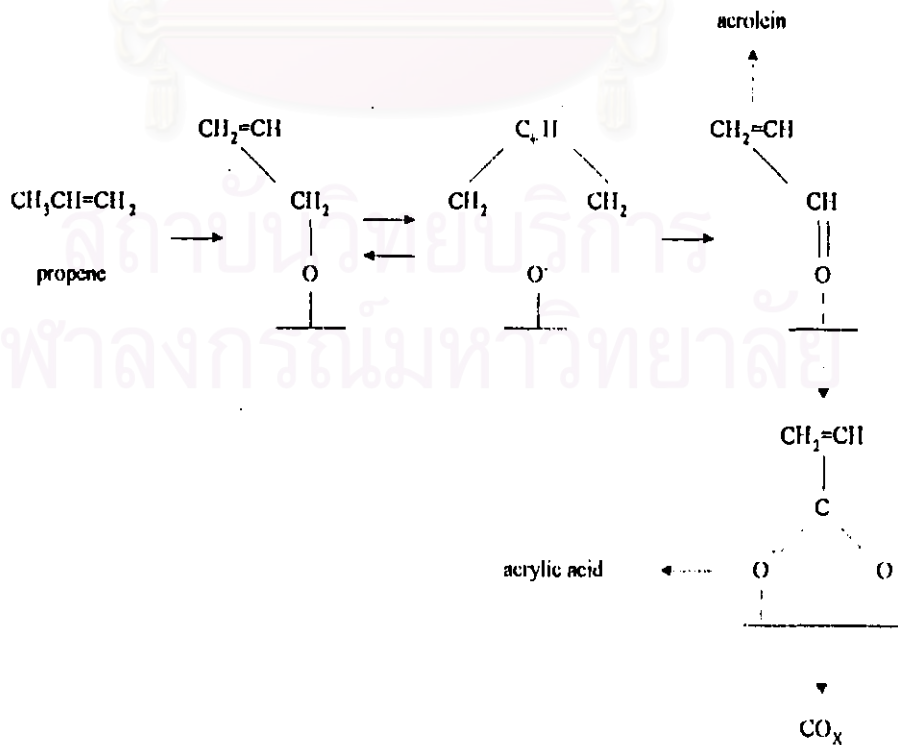


Figure 3.2 The oxidation path of propene over Co_3O_4 catalyst.

3.4 Surface reducibility and basicity

A general agreement is that the reducibility of the catalyst plays an important role in the reaction course on the activation of propane [Gao *et al.* (1994)]. In V-Mg-O catalysts, where one V atom is replaced by one Mg atom, the involved lattice V-O-M oxygen atom is less mobile and thus the catalyst surface is less reducible : these catalysts led to dominant propylene selectivity [Corma *et al.* (1993)]. The basic catalyst surface has also been [Owen *et al.* (1992)] to increase the alkene selectivity during the oxidative dehydrogenation of alkanes. Thus, on supported vanadium or molybdenum oxides, it was shown that incorporating alkaline metal decreased both the conversion of propane and the yields of products but increased the selectivity of propylene at the expense of the selectivity of the CO_x [Grabowski *et al.* (1995)]. The reason should be that basic surfaces facilitate the desorption of alkenes, more basic compounds than the corresponding alkenes, thus preventing them from further oxidation to carbon oxides. It could be the case of the V-Mg-O catalysts where the magnesia phase plays the role of basic centers during the propane partial oxidation to propylene [Chaar *et al.* (1987)].

In V-Mg-O systems, the reducibility of the catalyst was suggested to be important for the selectivity in oxidative dehydrogenation reaction of propane to propene. The less reducible of catalyst may be the important factor to increase alkene selectivity during the oxidative dehydrogenation of alkanes. For that reason, it may be possible to postulate the role of reducibility V-Mg-O systems to cover Co-Mg-O catalysts to explain the behavior of the formation of alkenes from alkanes.